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LIGHT-INDUCED ISOMERIZATION OF *o*-NITROTOLUENE IN WATER SOLUTION

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If *o*-nitrotoluene in water is exposed to ultraviolet light, a short-lived species is formed which has a strong absorption band in the blue and near ultraviolet regions of the spectrum. Two different absorption spectra of the species are given, interpreted as the absorption spectrum of the acid form and the anionic form of the species, respectively. The decay follows that of a first-order reaction with a rate constant of $0.76 \times 10^2 \text{ sec.}^{-1}$ for the acid and 1.0 sec.^{-1} for the anion.

Introduction

It recently was found in this Laboratory that *o*-nitrotoluene in solution on exposure to light undergoes a transformation to a short-lived colored state.² The decay of this colored state was found to follow the kinetics of a first-order reaction. In ethanol at room temperature ($24 \pm 1^\circ$) the half-life time was evaluated to be 5 msec.

Photochromism has been detected in compounds which are derivatives of *o*-nitrotoluene. Tschitschibabin and co-workers³ discovered that crystals of 2-(2',4'-dinitrobenzyl)-pyridine turn blue when

exposed to light and revert to the original colorless state in the dark. The solid has been extensively investigated over the last two decades⁴⁻⁷ but it has been found only recently by employing low temperatures that the color change can be brought about in solution.⁸ Also by employing low temperatures it has been found that other compounds closely related structurally, namely, 4-(2',4'-dinitrobenzyl)-pyridine⁹ and 2-(2'-nitro-4'-cyano-

(4) (a) K. Schofield, *J. Chem. Soc.*, 2408 (1949); (b) A. J. Nunn and K. Schofield, *ibid.*, 583 (1952).

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(6) H. S. Gutowsky and R. L. Rutledge, *J. Chem. Phys.*, **29**, 1183 (1958).

(7) B. M. Kuindshi, L. A. Igonin, Z. P. Gribova, and A. N. Shabadash, *Optics and Spectroscopy*, **12**, No. 2 (1962).

(8) R. Hardwick, H. S. Mosher, and P. Passailaigue, *Trans. Faraday Soc.*, **56**, 44 (1960).

(1) National Academy of Sciences-National Research Council Visiting Scientists Research Associate and Guest of the Massachusetts Institute of Technology associated with Prof. L. J. Heidt of the Department of Chemistry.

(2) G. Wettermark, *Nature*, **194**, 677 (1962).

(3) A. E. Tschitschibabin, B. M. Kuindshi, and S. W. Benewolskaja, *Ber.*, **58**, 1580 (1925).

benzyl)-pyridine¹⁰ are phototropic in solution as well.

Preliminary experiments in this Laboratory using flash photolysis have indicated that a variety of compounds, all being derivatives of *o*-nitrotoluene, are photochromic.² A closer study of the color change of *o*-nitrotoluene therefore has been undertaken and is reported in this article.

Experimental

Flash Apparatus.—A description of the flash apparatus will be given shortly by L. Lindqvist, Institute of Physical Chemistry, Uppsala University. Only some data pertinent to the actual experiments are given here. Briefly an electrical energy of 1800 joules (9 μ f., 20 kv.) was discharged through four straight quartz lamps symmetrically arranged around a cylindrical reaction vessel giving a flash duration of 5 μ sec. (1/e time). The reaction vessel had an optical path length of 20 cm. and was provided with an outer filter jacket which contained a 0.5 cm. layer of 50% aqueous acetic acid. This filter absorbed all light of wave lengths shorter than approximately 250 $m\mu$.

The light absorption changes in the system were recorded by means of a single beam absorption spectrophotometer. The monitoring lamp was a zirconium lamp (Sylvania K 100 Q) powered by a large bank of storage batteries. Other essential parts of the spectrophotometer consisted of a Bausch & Lomb small grating monochromator, an E.M.I. 9552B photomultiplier tube, and a Tektronix 535A oscilloscope. The slit width of the monochromator was kept constant (0.5 mm.), corresponding to a spectral band width of 3 $m\mu$. Various Corning color filters were used to cut off the secondary pass band from the grating of the monochromator. The anode current from the photomultiplier was amplified in a cathode follower mounted directly on the photomultiplier tube. The over-all circuit had a time resolution of about 5 μ sec. in the present experiments.

All experiments were carried out at room temperature (24 \pm 1°).

Solutions.—*o*-Nitrotoluene (Matheson Coleman & Bell) was recrystallized from absolute ethanol seven times. A simple apparatus¹¹ for low temperature recrystallization was used with Dry Ice and alcohol in the cooling bath. Further purification was obtained by passing an ethanol solution of the sample through a 60 cm. long column filled with aluminum oxide and collecting the middle fraction.

The concentration of *o*-nitrotoluene in the test solutions was 2×10^{-4} M. *o*-Nitrotoluene was mixed with absolute ethanol and diluted with aqueous 0.1 N NaOH and 1 N HCl, respectively. The final alcohol concentration amounted to 0.5% by volume.

Deaerating of Solutions.—Before each experiment the solution was carefully deaerated. The technique employed was to freeze, evacuate, and melt three times and to shake the solution in the presence of argon (Aircro for aluminum welding), then to freeze, evacuate, and melt three more times. The flask used for the deaeration was connected to the reaction vessel through a ground standard taper joint in such a way that the solution could be transferred without coming in contact with the stopcock grease.

Results and Discussion

Flashing a solution of *o*-nitrotoluene revealed that short-lived species (A^*) are formed which absorb strongly in the blue and near ultraviolet regions of the spectrum. A stable photo product (B) also is formed, as could be seen by a permanent change in the optical transmission of the solution. Scanning the spectrum over the region 300 to 600 $m\mu$ showed that the photo product (B) had an absorption band in the same region as A^* . Over the wave length region investigated the permanent (irreversible) increase in optical density on exposure

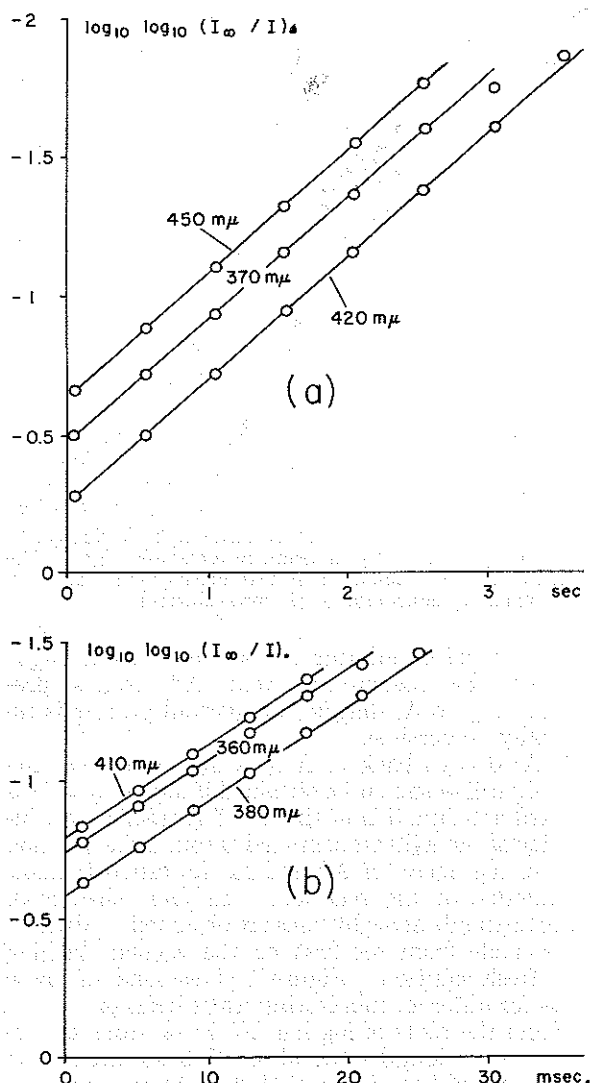


Fig. 1.—Plots of $\log \log (I_{\infty} / I)$ as a function of time for various wave lengths. (I is the intensity of the light transmitted through the solution during the fading of the short-lived species and I_{∞} the intensity after completion of the reaction.) (a) *o*-Nitrotoluene in 0.1 N NaOH; (b) *o*-nitrotoluene in 1 N HCl.

to a flash was less than 4% of the reversible change. When the same solution was flashed several times the response gradually weakened due to the accumulation of photo product. No effect on the rate of decay of A^* was observed even after extensive flashing (20–30 flashes). After about 20 flashes the degree of conversion of *o*-nitrotoluene into A^* was about half of that which was observed at the first flash. The portion of *o*-nitrotoluene converted to A^* in a flash could not be determined from these experiments.

The question arises whether the decay reaction of A^* constitutes the transformation of A^* into the new species B or the decay back to the original *o*-nitrotoluene (A) (or both).

As the photo product (B) has an absorption band in the same region as A^* it was impossible to measure the rate of formation of B by isolating a wave length where only B absorbed the light.

(9) H. S. Mosher, C. Souers, and R. Hardwick, *J. Chem. Phys.*, **32**, 1888 (1960).

(10) J. A. Sousa and J. Weinstein, *J. Org. Chem.*, **27**, 3155 (1962).

(11) A. L. Blum, *J. Chem. Educ.*, **35**, 200 (1958).

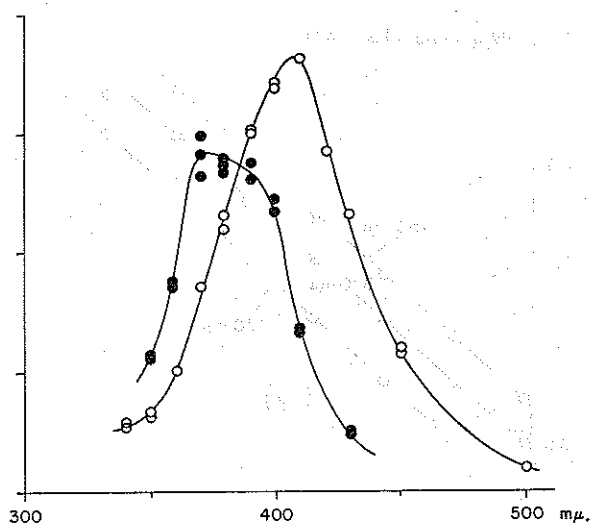


Fig. 2.—Absorption for *o*-nitrotoluene in 0.1 *N* NaOH (○) and 1 *N* HCl (●) after exposure to ultraviolet light. The ordinate is proportional to optical density with different proportionality constants for the two solutions.

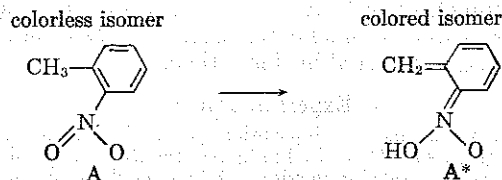
The available information on the system might support the assumption that A^* decays predominantly to A , that is, the over-all process is essentially reversible.

If A^* decays back to A in a first-order reaction a straight line should be obtained if $\log \log (I_\infty/I)$ is plotted as a function of time. (I symbolizes the intensity of the light transmitted through the solution during the decay of A^* and I_∞ the intensity after completion of the reaction.) In fact when such plots are made straight lines are obtained. All plots were made from the first or the second flashing of a fresh solution. Figure 1 gives some of these plots for different monitoring wave lengths.

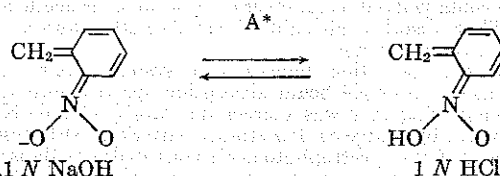
From the plots of $\log \log (I_\infty/I)$ vs. time at different wave lengths the absorption spectra of A^* in 0.1 *N* NaOH and in 1 *N* HCl could be calculated and are given in Fig. 2. It has been visualized³⁻¹² that the photochromism of 2-(2',4'-dinitrobenzyl)-pyridine is due to a proton transfer from the

(12) G. Wettermark, *J. Am. Chem. Soc.*, **84**, 3658 (1962).

$-\text{CH}_2-$ group to the 2'-nitro group together with a change in the structure of the aromatic ring to a quinoid configuration. It seems reasonable, therefore, to propose that the formation of A^* in *o*-nitrotoluene is described by the reaction



The colored isomer is probably a relatively strong acid. It is, however, reasonable to believe that in 1 *N* HCl mostly the acid is present. In 0.1 *N* NaOH the colored isomer should exist mostly as the anion.



One might thus conclude that the two spectra given in Fig. 2 are the spectrum of the anion (○) and the spectrum of the acid (●).

Table I gives the rate constants for the fading of A^* in 0.1 *N* NaOH and in 1 *N* HCl visualized as the fading of the anion and the acid, respectively. The data represent mean values obtained from all the plots of $\log \log (I_\infty/I)$ as a function of time for the different wave lengths (compare Fig. 1).

TABLE I
RATE CONSTANT FOR THE FIRST-ORDER FADING REACTION OF A^* AT ROOM TEMPERATURE ($24 \pm 1^\circ$)

Solution	Rate constant (sec. ⁻¹)
<i>o</i> -Nitrotoluene in 0.1 <i>N</i> NaOH (anion)	1.0
<i>o</i> -Nitrotoluene in 1 <i>N</i> HCl (acid)	0.76×10^2

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